Euro Hybrid Materials and Structures 2014
April 10 – 11

PFH – Private University of Applied Sciences,
Stade, Germany

EVALUATION OF SURFACE MODIFIED CFRP-METAL HYBRID LAMINATES

A. Monden[1*], M.G.R. Sause[1], A. Hartwig[1], C. Hammerl[2], H. Karl[1], S. Horn[1]

[1]University of Augsburg, Augsburg, Germany
[2]AxynTeC Dünnschichttechnik GmbH, Augsburg, Germany

ABSTRACT: The aim of this study was to evaluate the influence of different surface modification techniques on the bond strength between metal and carbon fibre reinforced polymers (CFRP). Sandwich specimens with a symmetrical layup consisting of unidirectional CFRP with a thin metal layer in the centre plane were investigated. To improve the fracture toughness of the CFRP-metal interface, various surface modification techniques like grit blasting, silane treatment and titanium dioxide coating were applied. Results were compared to adhesively bonded and untreated sandwich specimens. To measure the suitability of the surface modifications short-beam shear tests were used to determine the apparent interlaminar shear strength (ILSS) between CFRP and metal sheets. The displacement field on the side surface of the specimens was measured by digital image correlation techniques. This allows to assign signatures in the load-displacement profile to the occurrence of interlaminar failure. Each surface treatment resulted in a characteristic ILSS value, which was correlated to fracture surface morphologies. Grit blasted surfaces increased ILSS values, but interfacial failure was mainly adhesive. TiO_2 coating and silane treatment showed lower ILSS values, but higher degree of cohesive damage. Combinations of TiO_2 coating and silane treatment showed ILSS values almost identical to those of pure CFRP.

KEYWORDS: surface modification, fibre reinforced metal laminates, interlaminar shear strength

1 INTRODUCTION

Recent progress in the field of hybrid structures and materials has stimulated the need of mechanically and chemically stable joint technologies to combine fibre reinforced polymers (FRP) and metals. In aerospace applications, prominent examples for FRP-metal combinations are fibre reinforced metal laminates (FRML) like glass fibre/epoxy reinforced aluminium alloys (GLARE®) [1,2], aramid fibre/epoxy reinforced aluminium laminates (ARALL®) [3] or CFRP-titanium laminates [4-6]. While such combinations with lightweight metals are used in aerospace applications, steel is still the most widely used construction material in other fields of engineering, often due to economic reasons. Integration of structural FRP parts in such industrial areas leads inevitably to the challenge of joining these different material classes. Due to their different chemical structure, direct joints of steel and epoxy resin will result in poor adhesion, which leads to the requirement of surface treatment and modifications to achieve a mechanically and chemically stable joint [2,7,8]. To assess the effectiveness of different surface modification techniques on the bond strength between metal and epoxy resin, suitable testing geometries that allow evaluation of mode I (opening) or mode II (sliding) interfacial fracture toughness are necessary. To our knowledge no established standardized test methods exist for FRML for any of the mentioned delamination modes. Other researchers applied a variety of testing configurations to assess the bond strength between FRP and metals: Flexural test specimens with bonded CFRP strips, splice joint configurations for tensile tests [7], pull-out tests on CFRP-reinforced metal rods [9], adhesive test specimens incorporating a preformed crack [10], double strap joint tensile specimen [11], single lap joint and scarf joint tensile test specimen [12] and

* Corresponding author: Andreas Monden, Lehrstuhl für Experimentalphysik II, Universität Augsburg, Universitätsstr. 1, D-86135 Augsburg, Germany, Phone +49-[0]821-598-3407, Fax +49-[0]821-598-3411, andreas.monden@physik.uni-augsburg.de

double-notched shear specimens [13], just to name a few.
Main disadvantages of the mentioned testing methods are seen in the complex specimen preparation and the inability to compare the measured interfacial bond strength to the interfacial fracture toughness of pure FRP specimens.
Consistent with other authors [5,6] we prepared sandwich specimens with a symmetrical layup consisting of unidirectional CFRP with a thin metal layer in the centre plane. Short-beam shear (SBS) tests were conducted to determine the apparent interlaminar shear strength (ILSS) due to the high significance and low experimental complexity.
We chose the modified SBS test configuration to assess the suitability of different surface modification techniques to improve the fracture toughness between steel and fibre reinforced epoxy resin. Various modification techniques like grit blasting, silane treatment, titanium dioxide coating, adhesive bonding and a combination of titanium dioxide coating followed by silane treatment were applied to the metal surfaces.
In addition to improve bond strength between CFRP and metal, aim of the study is also to gain further insight into the interfacial failure behavior and to understand its dependence on surface microstructure and surface chemistry.

2 SURFACE MODIFICATIONS AND SPECIMEN PREPARATION

Sandwich plates were produced using a symmetrical layup consisting of 10 layers of SGL CE 1250-230-39 unidirectional epoxy-based prepreg with a nominal thickness of 0.22 mm per layer in cured state and X5CrNi18-10 steel foil of 0.1 mm nominal thickness laminated at the centre plane. A standard curing cycle using 130 °C temperature for 90 min following the materials supplier's recommendations was used. Different surface modifications were performed on 70 x 70 mm steel foils prior to curing them with the prepreg material.
We chose an "as received" rolled steel surface as reference. The steel surface was cleaned in an ultrasonic bath for 10 min in acetone, 10 min in isopropanol, 10 min in deionized water and then dried using pressurized, oil-free nitrogen.
Grit blasted surfaces with different roughness values were fabricated to examine the influence of mechanical interlocking and increased surface area on the interfacial fracture toughness. Sand blasting was performed using particle size distributions of 0 – 50 μm, 40 – 80 μm and 70 – 150 μm, respectively. Aluminium oxide abrasive with particle sizes of 106 – 150 μm was used to produce coarse surfaces. It is well known that initial adhesion levels can be significantly increased by suitable grit blasting variants [14]. The underlying principle is discussed in literature: increased effective area resulting in increased intermolecular bonding [15], modification of the surface topology enabling mechanical interlocking and at the same time crack deflection away from the interface into the bulk [16], as well as introduction of physicochemical changes yielding an increase of wettability [17].
Silane treatment was applied to the cleaned and degreased steel surfaces. 3-Glycidyloxypropyltrimethoxysilane ("Dynasilan® GLYMO", Evonik Industries AG) was hydrolyzed in aqueous solutions with concentrations of 0.5, 1, 2, 5 and 10 vol%, respectively. If required, pH-value was reduced to 5 by adding acetic acid. To promote hydrolyzation and silanol formation, stirring in an ultrasonic bath was performed for 10 min. The steel foils were then dipped into the solution for 10 min (first 5 min in ultrasonic bath). After removing the steel foils from the solution, excess liquid was blown off the surface using pressurized, oil-free nitrogen before drying and curing the surface for 10 min at 110 °C. The silanes form a layer on the metal oxide surface via covalent bonds. At the same time functional groups of the silane layer promote chemical bonds to the epoxy resin. In literature, the possibility of an interphase formation featuring an intermediate modulus between polymer and metal facilitating stress transfer is also mentioned [18,19].
Two titanium dioxide coatings of different thickness were prepared by reactive radio frequency (RF)-sputter technique. A titanium target (grade II) was used in 10 % oxygen containing argon plasma at a pressure of 0.01 mbar and sputter-power of 550 W. Before sputtering some substrates were cleaned in situ by using an argon plasma to remove unwanted weak oxide layers and thus improving interface toughness of the titanium dioxide layer. The thickness of the titanium dioxide coating was calculated to be 55 nm and 110 nm, respectively.
Combinations of titanium dioxide coating and subsequent silane treatment were examined. Titanium dioxide is known to be a stable metal oxide [20] and provides a high number of reactive sites for silanol deposition.
To compare the suitability of these surface modifications to the widely used film adhesive bonding, we also used the aerospace approved epoxy film adhesive "Cytec FM® 73" as reference. For this purpose, steel surfaces were grit blasted with aluminium oxide abrasive with particle sizes of 106 – 150 μm. After cleaning, the primer "Cytec BR® 127" was applied according to material supplier's instructions. Finally, the film adhesive was co-cured with the epoxy prepreg used.
Surface roughness values of the modified steel surfaces were measured using a surface profilometer of type "Veeco Dektak 6M Stylus" prior to laminating. Results of the arithmetic average roughness R_a and root mean squared roughness R_{RMS} are listed in table 1.

Table 1: *Roughness values of modified steel surfaces*

Surface modification technique	R_a [nm]	R_{RMS} [nm]
reference, untreated	180	225
sand blasted 0 – 50 µm	230	290
sand blasted 40 – 80 µm	258	319
sand blasted 70 – 150 µm	389	504
Al_2O_3 blasted 106 – 150 µm	995	1323
TiO_2 (55 nm)	206	252
TiO_2 plasma cleaned (55 nm)	168	312
TiO_2 plasma cleaned (110 nm)	146	179

In general, larger particle sizes lead to higher roughness values. The TiO_2 coating investigated shows similar surface roughness values as the reference, whereas pre-treatment via in situ plasma cleaning seems to reduce the roughness value R_a, but shows no clear trend regarding the roughness value R_{RMS}. Surface roughness values of silane coated surfaces were not measured as this treatment is assumed to have no effect on the topology.
After laminating and curing the sandwich plates, samples of 20 mm length, 10 mm width and 2.4 mm (3.0 mm for film adhesive bonded specimens) resulting thickness were cut from the cured laminate using a dry diamond saw cutting process to avoid preliminary delamination at the CFRP-metal interface due to moisture expansion or intake.

3 TESTING PROCEDURE

During short-beam shear (SBS) test, load is applied at the centre of the specimen utilizing a loading nose midways between the supports (Fig. 1).

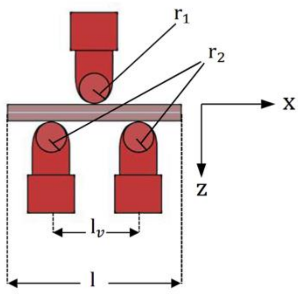

Fig. 1 *Schematic of short beam shear test configuration*

The apparent interlaminar shear strength (ILSS) value is calculated, which is related to the onset of delamination under shear forces parallel to the layers of the laminate:

$$\tau = \frac{3P_R}{4bh} \qquad (1)$$

τ: apparent interlaminar shear strength in [MPa]

P_R: load at the moment of delamination onset in [N]

b: width of the specimen in [mm]

h: thickness of the specimen in [mm]

Loading nose and support rollers with 3 mm radius were used and the support roller distance l_v was adjusted according to following relationship:

$$l_v = 5 \cdot \bar{h} \qquad (2)$$

$\bar{h}$: arithmetic mean thickness of the specimens in [mm]

Maximum shear stress is generated at the centre plane of the specimen [21] (Fig. 2).

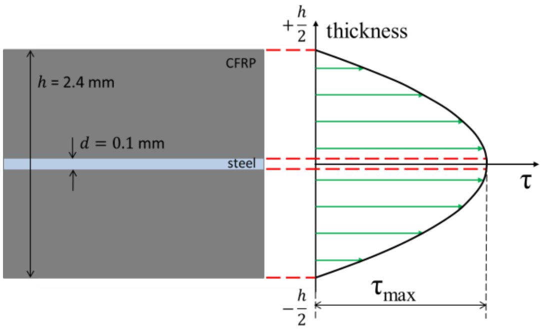

Fig. 2 *Parabolic shear stress distribution*

Thus, with the chosen sandwich configuration of a symmetrical layup containing a reasonable thin metal layer at the centre, interfacial failure is expected, as both metal-CFRP interfaces are located in the region of maximum shear stress.
During SBS test, samples were loaded with a constant displacement rate of the loading nose of v = 1 mm/min and at the same time the displacement field on the side surface of the specimens was measured by digital image correlation (DIC) techniques. The post-evaluation of these measurements allows to assign signatures in the load-displacement profile to the occurrence of interlaminar failure.
The two surfaces generated by delamination of the metal-CFRP interface generated during mechanical loading were carefully separated by use of a blade and optical microscopy was performed on the delaminated steel surface.

4 RESULTS

As shown for the untreated reference specimen in figure 3, DIC taken during SBS testing indicates failure of the CFRP-metal interface at the first signature of the stress-displacement curve (indicated by a red cross). The first signature coincides with delamination onset, which usually occurs at the region of maximum shear stress (near the centre plane of the specimen) and in between the lower supports. With delamination onset (and growth), the load drops to a lower value. As the bending stiffness of the specimen is reduced, the slope of the ascent after delamination onset decreases. Usually further load drops can be observed when loading the specimen further.

Failure of the sandwich specimens can be adhesive (delamination of the metal-CFRP interface) or cohesive (within the CFRP). The latter case indicates a bond strength of the CFRP-metal interface comparable or higher than that of pure CFRP.

The untreated reference specimens show low ILSS values with a large spread. This was found to be in good agreement with the results from optical microscopy, which reveal adhesive failure (delamination of the metal-CFRP interface). Adhering epoxy resin or fibre remnants to the metal interface are sparse (Fig. 4), indicating low bond strength between metal and CFRP.

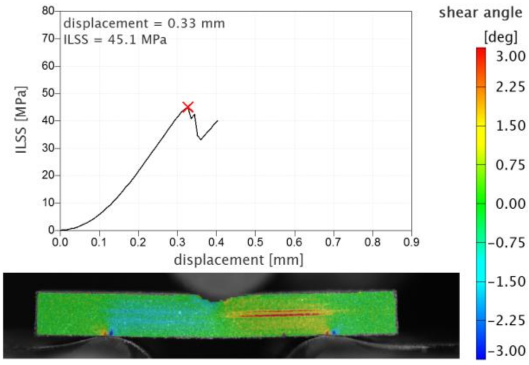

Fig. 3 *Representative DIC of untreated sandwich specimen*

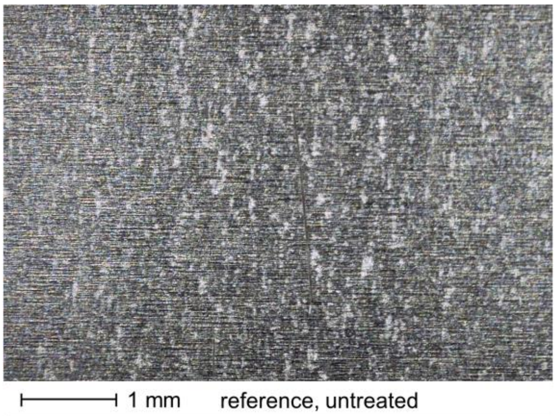

Fig. 4 *Representative microscopy image of delamination surface of untreated steel specimen*

Sand blasted and Al_2O_3 blasted specimen showed higher ILSS values and thus higher resistance to delamination. Still, optical microscopy did reveal mostly adhesive failure, since adhering fibre remnants can be observed only sporadically (Fig. 6).

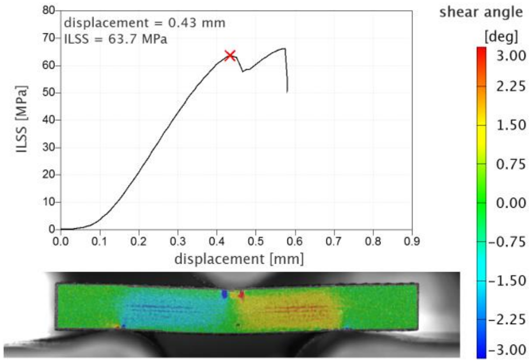

Fig. 5 *Representative DIC of Al_2O_3 blasted sandwich specimen*

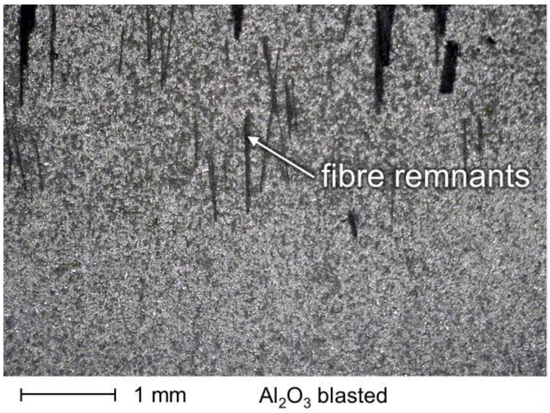

Fig. 6 *Representative microscopy image of delamination surface of Al_2O_3 blasted specimen*

Silane treatment increased delamination resistance, since increasing ILSS values were observed with increasing silane concentration. DIC taken during SBS testing indicates regions of adhesive (interfacial) and cohesive (within CFRP) failure (Fig. 7).

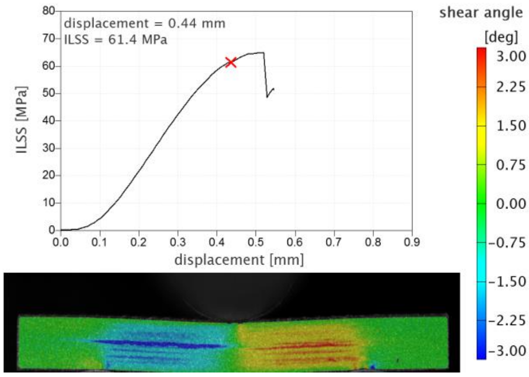

Fig. 7 *Representative DIC of silane treated (10 vol%) specimen*

Optical microscopy revealed an increasing ratio of cohesive failure of CFRP with increasing silane concentration. Figure 8 exemplarily shows the delamination surface of a 10 vol% silane treated specimen that is covered almost completely with resin and fibre remnants.

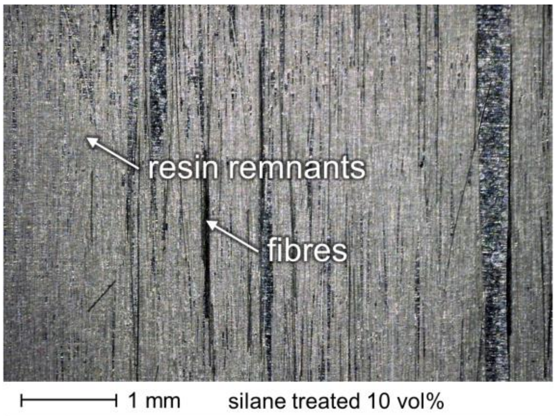

Fig. 8 *Representative microscopy image of delamination surface of silane treated (10 vol%) specimen*

Mechanical tests on TiO_2 coated specimens showed, that a stable metal oxide layer may improve adhesion between metal and epoxy resin. Surprisingly, in situ cleaning of the surface with argon plasma before sputtering seems to reduce delamination resistance, probably due to reduced surface roughness R_a. For both cases the large margin of error prevents a reliable conclusion. The thickness of the titanium dioxide coating seems to influence the delamination resistance. An increased thickness was found to increase ILSS values. Optical microscopy shows qualitatively similar results for all three TiO_2 coating variants tested (Fig. 10). For all samples regions covered with fibre and resin remnants as well as blank metal regions are observed.

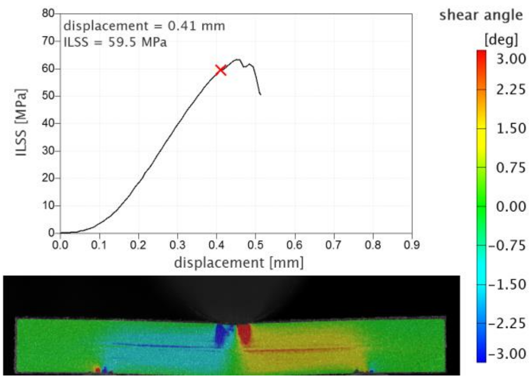

Fig. 9 *Representative DIC of argon plasma cleaned and titanium dioxide coated (thickness 55 nm) specimen*

Silane treatment of previously TiO_2 coated surfaces was found to yield even higher ILSS values than without silane treatment. The stable oxide surface provides a high number of reactive sites for silanol deposition.

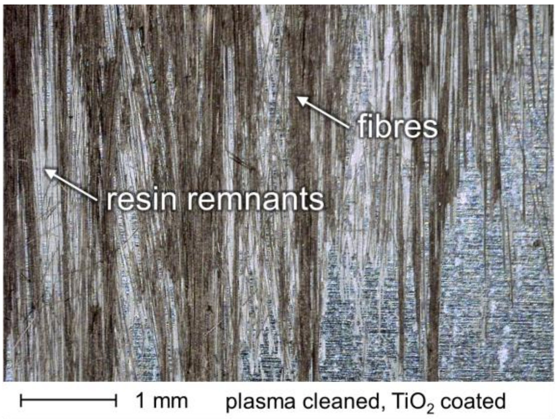

Fig. 10 *Representative microscopy image of delamination surface of argon plasma cleaned and titanium dioxide coated (thickness 55 nm) specimen*

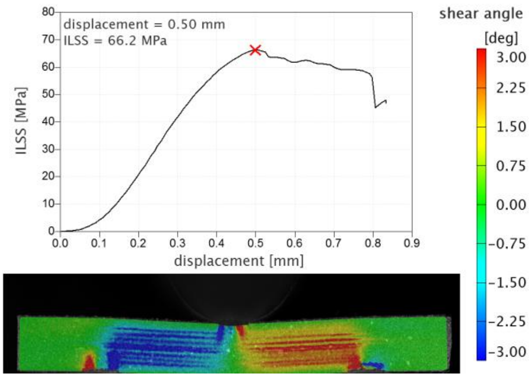

Fig. 11 *Representative DIC of argon plasma cleaned, titanium dioxide coated (thickness 55 nm) and subsequently silane treated (conc. 5 vol%) specimen*

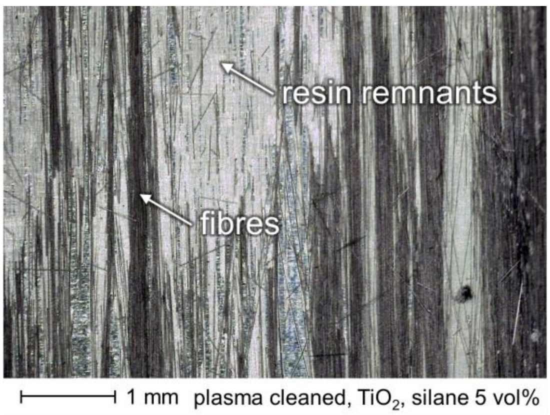

Fig. 12 *Representative microscopy image of delamination surface of argon plasma cleaned, titanium dioxide coated (thickness 55 nm) and subsequently silane treated (conc. 5 vol%) specimen*

As in the case of silane treatment of the pure metal surface, higher silane concentrations appear to increase adhesion. DIC results (Fig. 11) taken during SBS testing indicate values of interlaminar shear stresses comparable to those of pure CFRP. Inspection of the delamination surface reveals that the majority of the area consists of epoxy resin and fibres, indicating predominantly cohesive failure within CFRP (Fig. 12).

Bonding of CFRP and metal surface by adhesives only yields mediocre ILSS values. As revealed by DIC-analysis (Fig. 13), the adhesive layer was found to show plastic shear deformation over a wide range of deformation instead of brittle failure. No delamination was observed.

Measured ILSS values of the surface modified sandwich specimens in comparison to the untreated reference and CFRP are shown in figure 14.

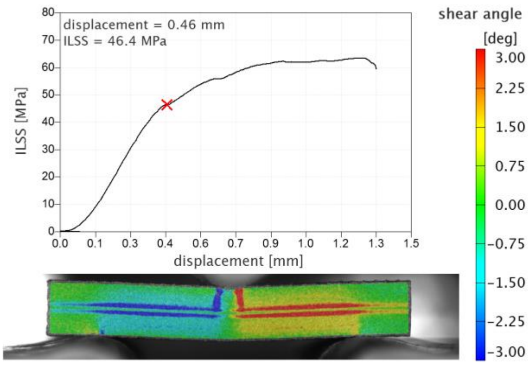

Fig. 13 *Representative DIC of adhesive film bonded specimen*

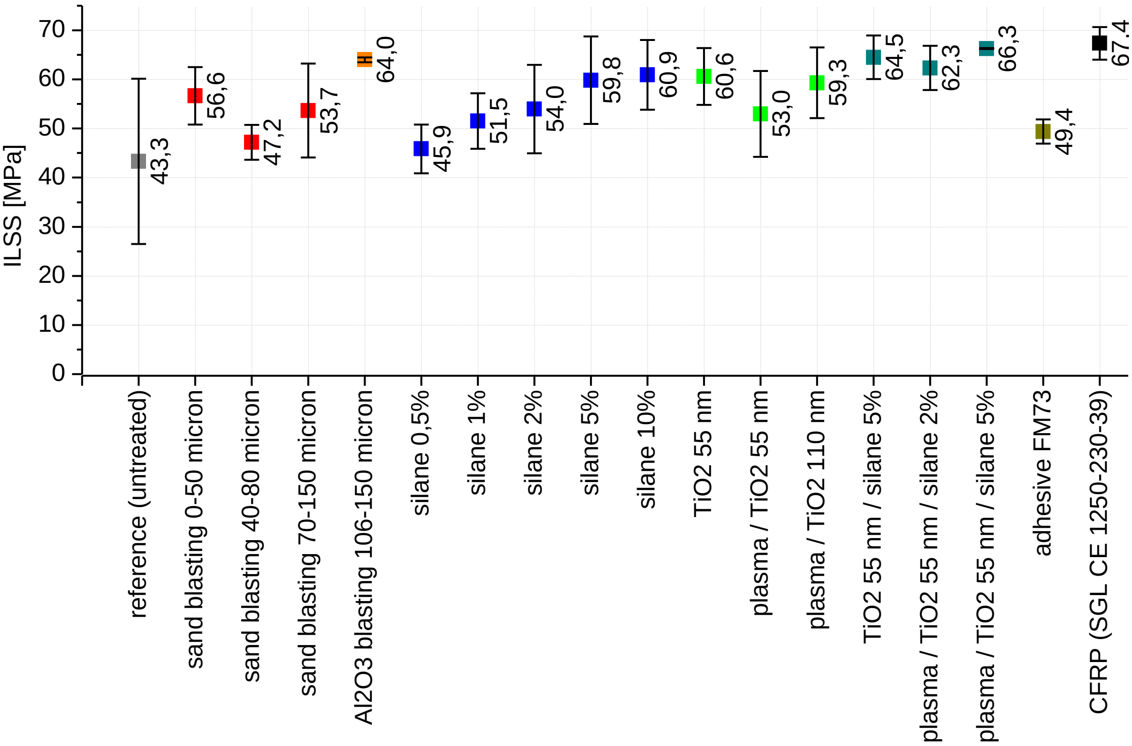

Fig. 14 *ILSS values of untreated sandwich specimens, surface modified sandwich specimens and CFRP*

5 CONCLUSIONS

We applied a variety of surface modification techniques to improve the interfacial failure behaviour in CFRP-metal sandwich specimens.

Compared to untreated specimen, all surface modification techniques were found to improve the bond strength between CFRP and steel. Al_2O_3 blasting increased the ILSS value significantly, indicating an improved initial delamination resistance, though microscopy revealed mainly adhesive failure of the CFRP-steel interface. Mechanical interlocking, effective surface area, surface energy and thus initial delamination resistance is increased due to the grit blasting process [14-17]. ILSS values of specimens that were treated with silane concentrations of 5 and 10 vol%, respectively, or were coated with titanium dioxide did show ILSS values lower than Al_2O_3 blasted specimens, but revealed higher degree of cohesive failure. Finally, titanium dioxide coating followed by silane treatment did improve ILSS values to 66.3 MPa, which is almost identical to values of pure CFRP samples (67.4 MPa). This indicates a significant improvement of the interfacial bond strength, which could be confirmed by optical microscopy, revealing mostly cohesive failure within the CFRP laminate. Film adhesive showed only a marginal increase of ILSS values compared to untreated specimens due to yielding at relatively low load levels. However, maximum ILSS was found to be comparable to pure CFRP. Moreover, large plastic shear deformation of the adhesive layer and more ductile failure behaviour was observed.

Though SBS tests proved suitable to demonstrate trends for the surface modifications examined and allowed consistent qualitative evaluation of the ILSS of hybrid laminates, a fracture mechanical approach, i.e. determination of mode I and mode II fracture toughness via double-cantilever beam (DCB) and 3-point end-notched flexure (3-ENF) tests is mandatory for a quantitative comparison. ILSS values obtained via SBS test are known to be unreliable with respect to their significance towards true interlaminar fracture toughness values. There is evidence that compressive stresses tend to supress interlaminar shear failure. For specimens without initial damage, the failure mode is essentially compressive buckling or yielding at regions near the loading nose [22], which was observable by the performed DIC measurements.

Further iterations and combinations of promising modification techniques are envisaged in further experiments, e.g. combining mechanical interlocking (grit blasting) with surface chemistry approaches (TiO_2 coating and silane treatment). Further, the influence of ageing in different environments (e.g. hot/wet environment) on the bonding strength of surface treated specimens is a key to understand the relationship between surface microstructure, surface chemistry and macroscopic failure behaviour.

6 ACKNOWLEDGEMENT

This work was conducted within the project “FORCiM³A – Forschungsverbund CFK/Metall-Mischbauweisen im Maschinen- und Anlagenbau“, which is funded by the Bayerische Forschungsstiftung (BFS). The authors take this opportunity to gratefully acknowledge the assistance and contributions of the former M.Sc. and B.Sc. students Kerstin Wagner, Benjamin Alaca, Sebastian Burger and Nora Schorer.

REFERENCES

[1] Meola C., Squillace A., Giorleo G., Nele L.: *Experimental Evaluation of an Innovative Glare Fibre Reinforced Metal Laminate in Pin Bearing*. Journal of Composite Materials, 37(17):1543-1552, 2003

[2] Sinmazçelik T., Avcu E., Bora M. Ö., Çoban O.: *A review: Fibre metal laminates, background, bonding types and applied test methods*. Materials and Design, 32(7):3671-3685, 2011

[3] Lawcock G., Ye L., Mai Y.-W.: *Novel Fiber Reinforced Metal Laminates for Aerospace Applications – A Review (Part I – Background and General Mechanical Properties)*. SAMPE Journal, 31(1):23-31, 1995

[4] Both J., Barfuß D., Baier H.: *Mode II Delamination of CFRP-Metal Laminates at Bolted Joints*. In: 18th International Conference on Composite Materials, 2011

[5] Kolesnikov B., Herbeck L., Fink A.: *Fortschrittliche Verbindungstechniken von Faserverbundstrukturen*. In: Deutscher Luft- und Raumfahrtkongress 2004, 1419-1428, 2004

[6] Wilmes H., Kolesnikov B.: *CFK/Titan, ein Hybridwerkstoff zur verbesserten Kopplung von Faserverbundstrukturen.* In: Intelligente Leichtbau Systeme 2002, 1-8

[7] Schnerch D., Dawood M., Rizkalla S., Sumner E., Stanford K.: *Bond Behavior of CFRP Strengthened Steel Structures*. Advances in Structural Engineering, 9(6):805-817, 2006

[8] Bischof C.: *ND-Plasmatechnik im Umfeld der Haftungsproblematik bei Metall-Polymer-Verbunden*. Materialwissenschaft und Werkstofftechnik 24:33-41, 1993

[9] Al-Mayah A., Soudki K., Plumtree A.: *Effect of Sandblasting on Interfacial Contact Behavior of Carbon-Fiber-Reinforced Polymer-Metal Couples*. Journal of Composites for Construction, 9(4):289-295, 2005

[10] Andrews E. H., King N. E.: *Adhesion of epoxy resins to metals*. Journal of Materials Science 11:2004-2014, 1976

[11] Liu H. B., Zhao X. L., Al-Mahaidi R.: *Effect of Fatigue Loading on Bond Strength between CFRP Sheets and Steel Plates*. International Journal of Structural Stability and Dynamics, 10(1):1-20, 2010

[12] Sato C., Ikegami K.: *Tensile Strength of Single Lap Joint and Scarf Joint between CFRP and Carbon Steel*. Journal of Adhesion 39:29-41, 1992

[13] Hinz S., Omoori T., Hojo M., Schulte K.: *Damage characterization of fibre metal laminates under interlaminar shear load.* Composites: Part A 40:925-931, 2009

[14] Critchlow G. W., Yendall K. A., Bahrani D., Quinn A., Andrews F.: *Strategies for the replacement of chromic acid anodizing for the structural bonding of aluminium alloys*. International Journal of Adhesion and Adhesives 26(6):419-453, 2006

[15] Sykes J. M.: *Surface Treatments for Steels*. In: “Surface Analysis and Pretreatment of Plastics and Metals”. Applied Science Publishers, 1982

[16] Shahid M., Hashim S. A.: *Effect of surface roughness on the strength of cleavage joints*. International Journal of Adhesion and Adhesives 22(3):235-244, 2002

[17] Harris A. F., Beevers A.: *The effects of grit-blasting on surface properties for adhesion*. International Journal of Adhesion and Adhesives 19:445-452, 1999

[18] Abel M.-L., Digby R. P., Fletcher I. W., Watts J. F.: *Evidence of specific interaction between γ-glycidoxypropyltrimethoxysilane and oxidized aluminium using high-mass resolution ToF-SIMS*. Surface and Interface Analysis 29(2):115-125, 2000

[19] Hobbs P. M., Kinloch A. J.: *The Computational Molecular Modelling of Organosilane Primers*. Journal of Adhesion 66:203-228, 1998

[20] Venables J. D.: *Review – Adhesion and durability of metal-polymer bonds*. Journal of Materials Science 19:2431-2453, 1984

[21] Selmy A. I., Elsesi A. R., Azab N. A., Abd El-baky M. A.*: Interlaminar shear behavior of unidirectional glass fiber (U)/random glass fiber (R)/epoxy hybrid and non-hybrid composite laminates*. Composites: Part B 43:1714-1719, 2012

[22] Whitney J. M., Browning C. E.: *On Short-Beam Shear Tests for Composite Materials*. In: V. International Congress on Experimental Mechanics, 1984